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NITION OF NORMAL PROPYL NITRATE BY COMPRESSION OF AIR—NORMAL

PROPYL NITRATE VAPOR MIXTURES

FC

17 MAY 1956

U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

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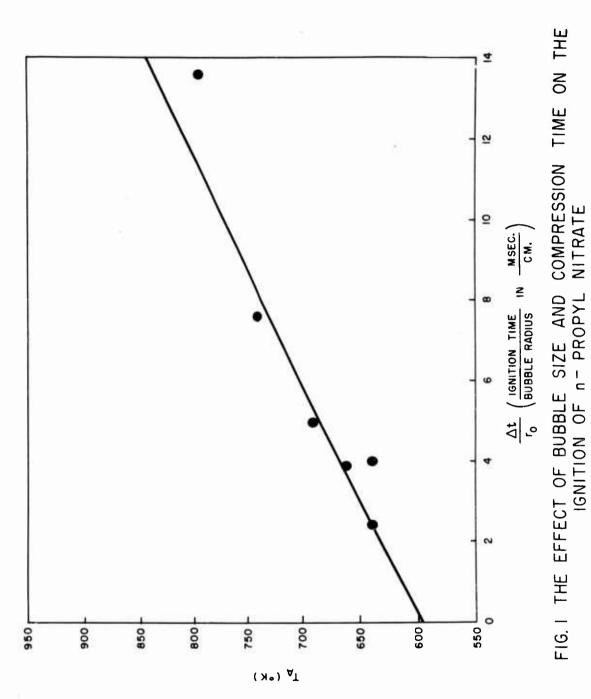Approved by Commander, U.S. NOL

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ILLUSTRATIONS

FIG. I THE EFFECT OF BUBBLE SIZE AND COMPRESSION TIME ON THE IGNITION OF n- PROPYL NITRATE

IGNITION OF NORMAL PROPYL NITRATE BY COMPRESSION
OF AIR-NORMAL PROPYL NITRATE VAPOR MIXTURES

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ABSTRACT: The ignition of liquid n-propyl nitrate
by the rapid compression of entrapped air bubbles has
been studied in a locked-stroke compressor. A minimum
bubble size for ignition under the particular conditions
has been observed and ease of ignition has been found to
increase with increasing bubble size. The results have
been analyzed in an approximate fashion.

U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

17 May 1956

The research reported herein was carried out under Task Assignment U1-6-253-12. Data has been obtained on the effect of bubble size on the ignitability of air-normal propyl nitrate vapor mixtures under rapid compression. This work was directed toward an understanding of the factors affecting the safe handling of normal propyl nitrate.

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IGNITION OF NORMAL PROPYL NITRATE BY COMPRESSION
OF AIR-NORMAL PROPYL NITRATE VAPOR MIXTURES

INTRODUCTION

As part of the program to study the hazards associated with the use of normal propyl nitrate (NPN) a study of the rapid compression of air-NPN vapor mixtures above liquid NPN was begun and the results obtained are reported here.

EXPERIMENTAL

The study was carried out in the locked-stroke compressor described in References (1), (2) and (3). In this compressor, a volume of gas is rapidly compressed by a piston driven by a larger piston under a predetermined initial pressure. At the end of the stroke the piston is locked in place, thus maintaining essentially constant volume, and hence constant pressure except for pressure drop due to cooling by the walls.

The pressure-time trace is recorded on an oscilloscope and the trace is photographed by means of a drum camera. Light emission is detected by a photomultiplier tube which "looks" through the window and shows up as a brightening of the pressure trace. The time at which light is emitted can thus be found.

For each experiment a U-tube closed at one end and containing liquid NPN was introduced into the working chamber of the compressor. An air bubble of controlled size was contained in the closed end of the U-tube. A layer of water was placed over the NPN in the open end of the U-tube. This was to prevent possible ignition of the NPN by the compressed helium used in the chamber.

The inside diameter of glass tubing used was 0.33-0.34 cm. The closure was formed by a square-cut piece of glass rod sealed into the end with a minimum of distortion; the length of the bubble was measured by a vernier caliper from the end of the glass rod to the bottom of the liquid meniscus.

1

A driving pressure of 180 psia was used on the large piston of the apparatus. A compression ratio of about 17:1 was obtained using a 0.25 in. spacer between the piston and the end of the chamber. Peak pressures in the range 700-800 psia were obtained, with compression times of 1-4 millisec.

RESULTS

The results are summarized in Table I. For runs 3-9, light emission was observed and this is interpreted as ignition occurring in the bubble. The U-tube was observed through the window at the end of the run while the chamber was still under pressure. In runs 3-9, there was evidence that some of the liquid has been consumed; this was especially noticeable for runs 7-9. For runs 1 and 2, no light emission or change in bubble volume was noted.

For the compressions during which light was emitted, that with initial volume of 0.056 cc gave a single maximum in light intensity near the peak pressure. Bubbles larger than this showed two maxima in the light intensity. The data obtained from the records were the pressure and time at which each ignition occurred and the peak pressure and total time of compression. These data are recorded in Table I. The pressure corresponding to the first ignition will be referred to hereafter as P_i and the peak pressure as P_f.

DISCUSSION

The points of interest in these results are that (a) ignition occurred in the gas phase but did not propagate through the liquid; (b) in some cases apparently two ignitions were observed; (c) the time interval before the first ignition decreased with increasing bubble size.

Points (a) and (b) suggest that the following occurred: The bubble was compressed until it became hot enough to ignite. The vapor then burned out. In the larger bubbles this occurred at a point fairly early in the compression stroke (in run 8, P_i = 377 psia vs P_f = 736 psia) so that there was time for more material to evaporate and be ignited. In the smaller bubbles the first ignition occurred close to the peak pressure (run 3, P_i = 790 psia vs P_f = 849 psia) so that there was time for only one ignition.

The failure of burning to propagate through the liquid may simply be due to the fact that the pressures attained were below the minimum pressure at which burning can be

2

TABLE I

COMPRESSION OF NPN-AIR ABOVE LIQUID NPN

Initial temp. 25°C, Initial pressure=1 atm.

Run	Initial Length (cm.)	Initial Volume (cc.)	1st light emission pressure psia (P_i)	time to 1st light emission (msec.)	2nd light emission pressure psia	time to 2nd light emission (msec.)	peak pressure (P_f) psia	time to peak pressure (msec.)
(1)	1.11	0.024	No light observed				693	3.08
(2)	.53	0.045	No light observed				Not measurable	
(3)	.62	0.056	790	3.24			849	3.70
(4)	.73	0.062	575	1.86	696	2.31	765	3.02
(5)	.80	0.077	Trace missed - evidence of propagation from bubble size					
(6)	.92	0.079	427	1.34	504	1.95	765	3.72
(7)	1.32	0.12	319	0.75	480	1.47	681	2.13
(8)	1.58	0.143	315	1.87	389	2.5	805	**
(9)	1.60	0.154	377	1.32	467	1.90	736	4.01

** Time of peak not estimated.

3

sustained in NPN in these tube diameters. No data is
available on the minimum burning pressures for NPN
burning in tubes and this aspect deserves study.

Qualitatively the fact that the interval before
ignition decreased with the increasing bubble size is
really an indication that for the larger bubbles the
compressions were more nearly adiabatic. This can be
demonstrated and the data treated in the following way.
Let the temperature at the instant of ignition for all
the cases be T_1 and let T_a be the temperature that would
have been reached at the ignition pressure if the process
had been adiabatic. The heat that the bubble has lost is

$$q = 4/3 \, \pi r_o^3 \, \rho_o \, (T_a - T_1) \, C_v \tag{1}$$

where r_o is the initial radius, the bubble being considered
spherical and of constant size, while ρ_o is the initial
vapor density in the bubble. Since $4/3 \, \pi r_o^3 \, \rho_o$ represents
the initial mass of the bubble, the above equation ignores
evaporation as a factor and is based on heat transfer by
conduction alone. This is an assumption of this treatment.

The heat transferred to the liquid may also be ex-
pressed by

$$q = 4 \pi r_o^2 h \left(\frac{T_1 - T_o}{2} \right) \Delta t \tag{2}$$

where Δt is the interval before ignition, h is the heat
transfer coefficient and T_o is the initial temperature;
$\frac{T_1 - T_o}{2}$ is thus an average temperature for the time Δt.

The assumptions implicit in equation (2) are that (a) h is
a constant (b) the bubble radius is a constant and is equal
to the initial value and (c) the temperature difference
between the bubble and the liquid may be adequately be
expressed by $1/2(T_1 - T_o)$. To replace these assumptions by
exact expressions would be enormously difficult. It seems
worthwhile to carry through the approximate treatment
bearing its limitations in mind and to see how well the
results may be interpreted. Equating (1) and (2) and
solving for $T_a - T_1$ results in

$$T_a - T_1 = 3/2h \, \frac{T_1 - T_o}{C_v \rho_o} \quad \frac{\Delta t}{r_o} \tag{3}$$

4

Since T_i is taken as a constant, equation (3) thus predicts that a plot of T_a vs. $\Delta t/r_o$ should be linear and intercept the ordinate axis at T_i.

For the calculation of T_a it is necessary to know C_v from which $C_p/C_v = \gamma$ can be found. The vapor pressure of NPN at 30° is 32.2 mm (5) so that the bubble composition would be

$$NPN = \frac{32.2}{760} = .042 \qquad Air = 0.958.$$

The heat capacity, C_v, for air may be calculated (4) as

$$C_v = 4.32 + 8.4 \times 10^{-4}\, T$$

while that for NPN may, as an approximation be taken as 36.4 cal/degree. (From the data of Gray et al. (6), C_v for ethyl nitrate is 29 cal deg.$^{-1}$mole^{-1}. The difference between the heat capacities for ethanol and n-propanol (7) is 7.4 cal. deg.$^{-1}$mole^{-1}. The value for n-propanol (7) is thus taken as $29 + 7.4 = 36.4$ cal deg.$^{-1}$mole^{-1}.) For the mixture then $C_v = 0.958 (4.32 + 8.4 \times 10^{-4}T) + 0.042 \times 36.4$; at 300°K $C_v = 5.99$ and $\gamma = 1.34$; at 1000°K $C_v = 6.47$ and $\gamma = 1.31$. A mean value of $\gamma = 1.33$ may then be taken and T_a calculated from the ignition pressures by

$$T_a = 298 \times \left(\frac{P_f}{P_o}\right)^{\frac{\gamma-1}{\gamma}}$$

The data are summarized in Table II for the six runs wherein ignition was observed and ignition pressures and times were recorded.

TABLE II

CALCULATED ADIABATIC TEMPERATURE AND COMPRESSION TIMES

Run	V_0	r_0	P_i	T_a	t	$\dfrac{\Delta t}{r_0}$
	cc	cm	psia	°K	msec	msec/cm
(3)	.056	0.239	790	799	3.24	13.68
(4)	.062	0.245	575	739	1.86	7.60
(6)	.079	0.266	427	688	1.34	5.04
(7)	.120	0.305	319	641	0.75	2.46
(8)	.143	0.322	315	638	1.26	3.90
(9)	.154	0.332	377	667	1.32	4.00

Figure 1 illustrates a plot of T_a vs $\Delta t/r_0$ and the points do fit a straight line. The value of T_i found from the intercept is 595°K.

The fact that at $\dfrac{\Delta t}{r_0} = 0$, $T_a = T_i$, shows that for these conditions the compression is truly adiabatic, i.e., the ignition temperature is the same as the calculated adiabatic temperature. There are two cases that fit these conditions, an infinitely large bubble $1/r_0 = 0$, and an infinitely fast compression $\Delta t = 0$. For all real cases, as the graph shows, $T_a > T_i$ and the difference measures the amount of heat lost, or the non-adiabaticity of the process.

The truly adiabatic compression of a bubble is, of course, the most favorable case for ignition. According to the above results the temperature that must be attained by such a compression if ignition is to occur is 595°K. Starting from 300°K this would require a compression of about 13 fold, e.g., from 1 to 13 atmospheres. Since all real compressions are in some measure non-adiabatic, this figure represents the minimum compression ratio necessary for ignition of the bubble. Any factor less than this would not yield ignition regardless of bubble size or compression rate.

This is an important result. The mathematical treatment has been approximate rather than rigorous and further studies are needed to test the conclusions drawn here. Such work is in progress at this Laboratory.

SUMMARY

The ignition of liquid n-propyl nitrate by the rapid compression of entrapped air bubbles has been studied in a locked-stroke compressor. The liquid has been contained in small (3.5 mm i.d.) glass U-tubes. Air bubbles ranging from 0.05 to 0.15 cc in volume have been trapped in the closed end of the U-tube and the system subjected to compression at the rate of about 20,000 atm. per second.

At bubble sizes greater than 0.05 cc ignition as evidenced by light emission has been observed. The time interval before ignition and the pressure at ignition have been found to decrease with increasing bubble size.

Making certain simplifying assumptions the data has been analyzed. From this treatment an ignition temperature of 595°K for NPN-air bubbles has been found, corresponding to a compression ratio of about 13:1 for the ideal, perfectly adiabatic compression. For compressions having a compression ratio less than this, the analysis used predicts that ignition will not occur regardless of bubble size or compression rate.

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